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COMPLETE SPECIFICATION  
Process for the Purification of Lactams

SPECIFICATION NO. 1,002,424

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are:— Horst Metzger, Dieter Weiser and Helmut Doerfel, citizens of the Federal Republic of Germany, residing, respectively, at 80 Wittelsbachstrasse, Ludwigshafen/Rhein; 14 Berliner Strasse, Ludwigshafen/Rhein; and 7 Edenkobener Strasse, Ludwigshafen/Rhein; Federal Republic of Germany.

THE PATENT OFFICE

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1      furic acid, or by catalytic means. Caprolactam can also be obtained according to a process disclosed in British Patent Specification 904,302 by the action of nitrosating agents in 20 sulfuric acid on cyclohexane carboxylic acid.

25      Experience has shown that each of the above-mentioned processes gives rise to more or less impure products which are difficult to purify and which cannot be recovered in a satisfactory condition even by fractional distillation or sublimation. On polymerization, the impurities in the lactams have a deleterious effect on the polymers and lower their quality. The polymers possess a high "colour value". 30      Apart from this, the quality of the lactams often deteriorates rapidly during storage.

35      Among other criteria, the colour rating is principally used to assess the purity of a lactam. The determination of the colour rating in accordance with the Hazen scale is effected by comparing the polylactam melt with standard solutions which have been prepared by dissolving known amounts of potassium hexachloroplatinate and cobalt chloride in an aqueous solution of hydrochloric acid. Thus, a colour rating of 500 Hazen units (= APHA units) corresponds to that of a solution of 1.25 g potassium hexachloroplatinate (IV),  $K_2PtCl_6$ , (equivalent to 0.500 g Pt) and 1 g

stances is recommended for the prevention of yellowing during storage. In another purification process, the lactam is washed out with salt - saturated alkali solution. It is further known to treat lactams with an inert gas, e.g., molecular hydrogen, in the presence of small amounts of an alkaline or acid substance. These processes are more or less economically and technically expensive, difficult to carry out and often lead to large losses of lactam. Furthermore, some of these processes are not consistent or are not generally applicable, and can therefore only be used for certain lactams or for lactams of a given origin.

It has now been found that a satisfactory purification of lactams having 4 to 12 carbon atoms, can be achieved by treatment with hydrogen in a process which comprises contacting the lactams either dissolved in an inert solvent or liquified, in the presence of basic reacting substances, with nascent hydrogen formed *in situ* or with molecular hydrogen, in the presence of hydrogenating catalysts under such conditions that the lactams are substantially unattacked.

According to the present invention, any lactams containing 4 to 12 carbon atoms, e.g., pyrrolidone, valerolactam, caprolactam, enantholactam, caprylolactam or laurolactam,

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## COMPLETE SPECIFICATION

### Process for the Purification of Lactams

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for purifying lactams.

Lactams are valuable raw materials in the manufacture of polyamides. Lactams can be produced in the well-known manner from the corresponding oximes or salts thereof by means of the Beckmann conversion using sulfuric acid, or by catalytic means. Caprolactam can also be obtained according to a process disclosed in British Patent Specification 904,302 by the action of nitrosating agents in sulfuric acid on cyclohexane carboxylic acid.

Experience has shown that each of the above-mentioned processes gives rise to more or less impure products which are difficult to purify and which cannot be recovered in a satisfactory condition even by fractional distillation or sublimation. On polymerization, the impurities in the lactams have a deleterious effect on the polymers and lower their quality. The polymers possess a high "colour value". Apart from this, the quality of the lactams often deteriorates rapidly during storage.

Among other criteria, the colour rating is principally used to assess the purity of a lactam. The determination of the colour rating in accordance with the Hazen scale is effected by comparing the polylactam melt with standard solutions which have been prepared by dissolving known amounts of potassium hexachloroplatinate and cobalt chloride in an aqueous solution of hydrochloric acid. Thus, a colour rating of 500 Hazen units (=APHA units) corresponds to that of a solution of 1.25 g potassium hexachloroplatinate (IV),  $K_2PtCl_6$ , (equivalent to 0.500 g Pt) and 1 g

cobalt chloride,  $CoCl_2 \cdot 6 H_2O$  in 100 ml concentrated hydrochloric acid made up to 1000 ml with water. The lower colour ratings are obtained by appropriate dilution of this solution.

Various processes are known for the purification of lactams, especially  $\epsilon$ -caprolactam, obtained by the conversion of cycloaliphatic ketoximes. Thus, lactams can be purified, for example, by recrystallization, by treatment with ion exchangers catalytic atmospheric oxidation or by treatment with hydrogen in the presence of a hydrogenating catalyst (British Patent Specification No. 778,751). The addition of basic substances is recommended for the prevention of yellowing during storage. In another purification process, the lactam is washed out with salt-saturated alkali solution. It is further known to treat lactams with an inert gas, e.g., molecular hydrogen, in the presence of small amounts of an alkaline or acid substance. These processes are more or less economically and technically expensive, difficult to carry out and often lead to large losses of lactam. Furthermore, some of these processes are not consistent or are not generally applicable, and can therefore only be used for certain lactams or for lactams of a given origin.

It has now been found that a satisfactory purification of lactams having 4 to 12 carbon atoms, can be achieved by treatment with hydrogen in a process which comprises contacting the lactams either dissolved in an inert solvent or liquified, in the presence of basic reacting substances, with nascent hydrogen formed *in situ* or with molecular hydrogen, in the presence of hydrogenating catalysts under such conditions that the lactams are substantially unattacked.

According to the present invention, any lactams containing 4 to 12 carbon atoms, e.g., pyrrolidone, valerolactam, caprolactam, enantholactam, caprylolactam or laurolactam,

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can be purified, regardless of the manner by which they have been prepared. Furthermore, the lactams are recovered with practically no loss. The invention may be carried out, 5 where necessary, after neutralization and/or after filtering off solid components, distillation or sublimation. On subsequent polymerization, products are produced which are satisfactory in all respects and which have an excellent colour rating. The monomeric lactams also have satisfactory storage - stability characteristics. 10

The basic materials mainly employed are inorganic bases. The basic materials are used 15 in quantities of from 0.01 to 20, especially from 0.1 to 10 percent by weight based on the weight of the lactam. Larger amounts of basic material can be used, but are generally avoided for economical reasons. Suitable inorganic bases are in particular alkali metal hydroxides, alkali metal oxides, alkali metal carbonates and alkali metal bicarbonates, e.g., sodium or potassium hydroxide, sodium carbonate, sodium bicarbonate and sodium oxide. 20

Use can also be made of alkali metal salts of fatty acids with 1 to 4 carbon atoms, alkaline earth metal hydroxides, oxides, or carbonates such as sodium acetate, calcium hydroxide, barium hydroxide, calcium oxide and calcium 25 carbonate, as well as ammonia and alkyl derivatives, i.e., mono-, di-, and tri- alkylamines with 1 to 4 carbon atoms in the alkyl radical. In a given case, preference is given to one or the other basic substance, after 30 first having determined by prior trials the most effective base in the given instance, and also the quantity required. It is also readily possible to establish by means of preliminary 35 trials whether a given base might advantageously be neutralized before working up the lactam solution, which may be based on water, for recovery of the lactam, e.g., by distillation.

The hydrogen to be used in the purification 40 of the lactam must be activated. This can be accomplished by generating the hydrogen in the reaction mixture itself, i.e., by employing it in the "nascent" state, or by allowing molecular hydrogen to act on the lactam in the presence of hydrogenation catalysts. It is also possible to work with a combination of both methods of activation, that is, with nascent hydrogen in the presence of a hydrogenation catalyst. 45

In purifying lactams with nascent hydrogen in accordance with the present invention, all processes in which nascent hydrogen is generated in an alkaline medium are suitable provided that the lactam is not attacked, or only slightly so, under the conditions of the reaction. Examples of such processes are provided by the reactions between Raney alloys and alkaline solutions; between hydrazine or its hydrate and Raney nickel, Raney cobalt, Raney nickel 50 alloys, palladium or platinum; between low

molecular alkanols, e.g., with 1 to 5 carbon atoms, or cycloalkanols with 5 to 8 carbon atoms, and sodium amalgam or sodium; between water and sodium amalgam or sodium; and even between zinc dust and water or caustic soda, preferably in the presence of catalytic quantities, i.e., from 0.001 to 10, in particular 0.01 to 1 percent of hydrogenation catalysts, such as palladium, platinum or Raney metals, with reference to the lactam. 55

The minimum amount of hydrogen-generating reagent required for the purification of lactams with "nascent" hydrogen in an alkaline medium, differs from reagent to reagent, and can also differ from lactam to lactam, depending on its source. However, the optimum amounts can be determined very easily by prior trials. In general, considerably less than molar quantities of reagent or catalyst are required per mole of lactam, but larger amounts do not usually have any deleterious effect. A large excess is, of course, undesirable on economic grounds, hence quantities of hydrogen - generating reagents are preferred which produce from about 0.001 to 0.5, in particular 0.001 to 0.2 moles hydrogen per mole lactam. 60

The reaction temperatures and times are dependent upon the process used for producing the nascent hydrogen and upon the particular lactam being treated. The most favorable conditions can, however, be readily determined by prior trials. Generally speaking, working temperatures of between 50 and 100°C. are recommended, but lower or higher temperatures in the range between - 15 and + 250°C. can be employed. 65

In the majority of cases, the purification of the lactam should reach completion within not more than 5 hours treatment with hydrogen; often 30 to 60 minutes suffices, but even shorter times, e.g., 15 minutes may be adequate. 70

In carrying out the purification of lactams in accordance with the invention by treatment with nascent hydrogen in an alkaline medium, a useful procedure is to dissolve the lactam in water or in an inert organic solvent, e.g., an alkanol with 1 to 4 carbon atoms, such as methanol, ethanol, propanol, or a cycloalkanol with 5 to 8 carbon atoms, such as cyclohexanol, or in a mixture of water with water miscible inert organic solvents, for example, with water - miscible open - chain or cyclic ethers such as dioxan, tetrahydrofuran, glycol monomethyl ether, or diglycol ether. The basic reacting substance is added to the solution, and hydrogen is generated according to one of the previously mentioned processes, preferably at an elevated temperature, e.g., up to the boiling point of the solvent used but not higher than 250°C. The order in which the individual reactants are added can be varied provided that not too long a time is allowed to elapse between the 75

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addition of the various components. Generally, lactam solutions of 20 to 80 percent by weight are employed. After the hydrogen treatment has been completed, and, should it be desired, after neutralization of the basic substance and filtration of solid particles, the solvent is removed, e.g., by distillation. Thereupon the lactam left behind can be isolated in a pure form by further distillation or sublimation in vacuo.

Another form of the process according to the invention consists in treating the lactam, or its solution in an alkaline medium, with catalytically activated hydrogen. Suitable catalysts in this case are conventional hydrogenation catalysts which however, owing to the conditions chosen, do not hydrogenate the lactam or, at least, only slightly so. These include the hydrogenation catalysts usually employed, viz., metal catalysts such as palladium, platinum, nickel or ruthenium, and also the noble metal oxides such as palladium oxide or platinum oxide which can, if desired, be reduced before being used as catalysts. The catalysts may be supported on carriers, e.g., on activated carbon, pumice, silica, aluminum oxide, barium sulphate, calcium carbonate, magnesium silicate, or magnesium oxide. Very suitable as catalysts are the Raney catalysts, e.g., Raney nickel, cobalt or copper.

The catalysts can be suspended in the lactam solution either in a fine granular form or in powder form. In this event, it is of advantage to separate the catalyst from the solution after concluding the hydrogenation, e.g., by filtration. This removal is not necessary when, as in the case of continuous operation, the catalyst is present in a coarse granular form in a stationary catalyst layer in the reaction chamber, while the lactam solution and hydrogen are passed in a continuous manner, where necessary in counter-current, through the reaction chamber.

The amount of hydrogenation catalyst required for carrying out the purification of lactams in accordance with this invention, can vary within wide limits. It is dependent on the catalyst itself, and on the lactam and the reaction conditions desired. The amount can easily be established from case to case by prior trials. In general, an amount of 0.1 to 5 percent catalyst with reference to the weight of lactam is adequate, but larger quantities do no harm.

The process can be conducted either at atmospheric pressure or at an increased pressure of, e.g., 1 to 300 atmospheres.

The treatment of the lactam or its solution can be effected either at room temperature or at an elevated temperature, a much shorter reaction time being required at the higher temperature. This difference is very pro-

nounced when using, for example, platinum or ruthenium catalysts, and it is often advisable to carry out the process at a temperature which is only slightly below the boiling point of the lactam or the solvent. In general, temperatures between about 0 to 120°C. are employed.

In carrying out the process of the invention in this form, the lactam, dissolved in water or in some other inert solvent, as previously described in detail, can be subjected to treatment in the presence of a suitable base and a suitable hydrogenation catalyst, at room temperature or at an elevated temperature, if necessary under pressure, until such time as no more hydrogen is taken up or the rate of absorption of hydrogen has fallen considerably. No reduction of the lactam to imine was observed under the conditions described.

After treatment with hydrogen and where necessary, after neutralization and/or filtration and perhaps removal of solvent, the reaction mixture is subjected to distillation or sublimation, and the purified lactam is thus recovered.

The process is described in greater detail in the following Examples, but these Examples are by no means intended to limit the scope of the invention. The amounts given are parts by weight unless otherwise indicated; parts by weight and volume stand in a relationship of gram to cubic centimeter.

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#### EXAMPLES 1 to 16

100 parts of a caprylolactam manufactured by the sulfuric acid conversion of a cyclooctanone oxime hydrochloride, the latter having been prepared by photo-oximation, are dissolved in 500 parts water, and to this solution are added the amounts of basic substance and reagent set forth in the accompanying table (Table 1); the mixture is heated with stirring for the time shown and at the temperature indicated. After completion of the reaction the pH value is adjusted to 7 by means of dilute sulfuric acid, and the reaction mixture is filtered. Water is first removed from the filtrate by distillation under reduced pressure, and the lactam is then distilled at 0.5 mm Hg. The first 5 parts are allowed to run off. The main fraction (b.p. 112°C. at 0.5 mm Hg) is treated with 3 parts hexamethylene diammonium adipate under an atmosphere of nitrogen in a glass tube of 18 mm internal diameter for 6 hours at 260 to 270°C. to effect the condensation to polycaprylolactam. After completion of polymerization, the polymer colour ratings are measured in accordance with the Hazen scale. The results are given in the last column of Table 1.

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TABLE 1

| Example No. | Base (parts) | Reactants (parts)                                    | Reaction Temp. °C. | Reaction Time in min. | Polymer Colour Rating |
|-------------|--------------|--|--------------------|-----------------------|-----------------------|
| 1           | 2 NaOH       | 1 Hydrazine hydrate + 0.5 Raney—Ni                   | 90—100             | 30                    | 40—60                 |
| 2           | 5 NaOH       | 5 Hydrazine hydrate + 1.5 Raney—Co                   | 90—100             | 60                    | 40—60                 |
| 3           | 5 KOH        | 5 Hydrazine hydrate + 1.0 Raney—Ni alloy             | 90—100             | 60                    | 40—60                 |
| 4           | 2 NaOH       | 1 Raney—Ni alloy                                     | 90—100             | 60                    | 40—60                 |
| 5           | 1 NaOH       | 1 Raney—Ni alloy                                     | 90—100             | 60                    | 60                    |
| 6           | 1 NaOH       | 0.5 Raney—Ni alloy                                   | 90—100             | 60                    | 60—80                 |
| 7           | 1 NaOH       | 0.5 Raney—Ni alloy                                   | 90—100             | 30                    | 80—100                |
| 8           | 5 NaOH       | 1 Raney—Ni alloy                                     | 50                 | 60                    | 80—100                |
| 9           | 5 NaOH       | 5 Hydrazine hydrate + 2 Pd on BaSO <sub>4</sub> (1%) | 90—100             | 60                    | 60—80                 |
| 10          | 10 NaOH      | 10 Zn dust   | 80                 | 180                   | 150                   |
| 11          | 10 NaOH      | 10 Zn dust + 0.5 Raney—Ni                            | 80                 | 180                   | 60—80                 |
| 12          | 10 NaOH      | 10 Zn dust + 1 Pd on carbon (5%)                     | 90—100             | 60                    | 40—60                 |
| 13          | 2 NaOH       | 40 Sodium amalgam (5%)                               | 90—100             | 300                   | 100                   |
| 14          | —            | Blank test with water                                | 90—100             | 60                    | 350                   |
| 15          | 10 NaOH      | —  | 90—100             | 60                    | 350                   |
| 16          | 10 NaOH      | —  | 90—100             | 180                   | 350                   |

**EXAMPLE 17**

100 parts caprolactam manufactured by the sulfuric acid conversion of cyclohexanone oxime, the latter having been prepared by photo-oxidation, are dissolved in 400 parts water, and to this solution are added 2 parts sodium hydroxide, 2 parts hydrazine hydrate and 0.5 parts Raney nickel. This mixture is heated with stirring for 1 hour at from 90 to 100°C. The mixture is then filtered, and, without neutralizing, water is distilled off from the filtrate under reduced pressure, followed by caprolactam under a pressure of 0.5 mm Hg. The first 5 parts are allowed to run off. The principal fraction (b.p. 105°C. at 0.5 mm Hg) is then further treated in the manner described in Example 1. The caprolactam thus obtained has a polymer colour rating of from 40 to 60.

In comparison experiments, in which caprolactam is treated only with water or water and sodium hydroxide, polymer colour ratings of respectively 350 or from 300 to 350, are obtained.

**EXAMPLE 18**

100 parts of a once-distilled caprolactam manufactured according to a process disclosed in British Patent Specification 904,302 by the action of nitrosyl sulfuric acid and oleum on cyclohexane carboxylic acid are dissolved in 400 parts water, and 2.0 parts sodium hydroxide and 1.0 part Raney nickel alloy are added; the mixture is then heated with stirring for 60 minutes at from 90° to 100°C. After this, the pH value of the solution is adjusted to 7 by means of dilute sulfuric acid, and the solution filtered. Water is removed from the filtrate under reduced pressure and the caprolactam is then distilled under pressure of 0.5 mm Hg. The first 5 parts are allowed to run off. The principal fraction (b.p. 105°C. at 0.15 mm Hg) is further treated in the manner described in Example 1. The product has a polymer colour rating of from 40 to 60.

In comparison experiments, in which caprolactam is treated only with water or water and sodium hydroxide, polymer colour ratings of respectively 350 or from 300 to 350, are obtained.

**EXAMPLE 19**

100 parts caprylolactam, manufactured from cyclooctane carboxylic acid by the action of nitrosyl sulfuric acid and oleum, are dissolved in 380 parts water; to this solution are added 2 parts sodium hydroxide, 1.0 part hydrazine hydrate and 0.5 parts Raney nickel, and the mixture is heated with stirring for 1 hour at 90 to 100°C. After this, the solution is neutralized with dilute sulfuric acid and then filtered. Water is first removed from the filtrate by distillation under reduced pressure, and the caprylolactam is then distilled off at a pressure of 0.5 mm Hg. The first 5 parts are allowed to run off. The principal fraction (b.p. 112°C. at 0.5 mm Hg) is then further treated in the manner described in Example 1; the product has a polymer colour rating of 40.

In comparison experiments, in which caprylolactam is treated only with water or water and sodium hydroxide, polymer colour ratings of respectively 350 or 300 to 350, are obtained.

**EXAMPLE 20**

100 parts caprolactam, manufactured by the catalytic conversion of cyclohexanone oxime, are dissolved in 400 parts water. 2.0 parts sodium hydroxide and 1.0 part Raney nickel alloy are added, and the mixture heated with stirring for 60 minutes at 100°C. The procedure is continued as described in Example 1, the distillation of the main fraction at 105°C. under 0.5 mm Hg yielding 94.0 parts caprolactam with a m.p. 70°C. On further treating in accordance with Example 1, the product exhibits a polymer colour rating of 60.

In comparison experiments, in which caprolactam is treated only with water or water and sodium hydroxide, polymer colour ratings of respectively 350 or from 300 to 350, are obtained.

**EXAMPLE 21**

40 parts of a caprolactam which has been obtained by the Beckmann conversion of cyclohexanone oxime in sulfuric acid and once-distilled, and which cannot be further purified by repeated distillation, are dissolved in 100 parts water. To the solution are added 0.5 parts potassium hydroxide and then 3 parts Raney nickel. On shaking with hydrogen, at 20°C. and under atmospheric pressure, 50 parts by volume hydrogen are taken up in the course of 40 minutes. Thereupon, the hydrogenation is discontinued, the solution filtered, and the filtrate distilled under a pressure of 14 mm Hg. On distilling the residue at a reduced pressure, and after running off the first two parts, which consist essentially of caprolactam, 37.8 parts caprolactam, b.p. 105°C. at 0.5 mm Hg (m.p. 70°C.), corresponding to a 94.4 percent main fraction referred to the initial weight of impure lactam were obtained. The polycaprolactam obtained after polymerization as described in Example 1, has a colour rating of 40 to 60.

If impure lactam is treated in a similar manner but without the addition of alkali, the polymerization product obtained from the processed lactam possesses a colour rating of 350. Similarly, treatment with hydrogen without catalyst, but in the presence of potassium hydroxide yields a product with a colour rating of 350.

**EXAMPLE 22**

50 parts of a once-distilled caprolactam, obtained by the catalytic conversion of cyclohexanone oxime, are dissolved in 100 parts water and, after the addition of 2 parts sodium

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hydroxide and 0.5 parts pre-reduced PtO<sub>2</sub>, shaken with hydrogen at 21°C. under normal pressure, 1295 parts by volume hydrogen are taken up in the course of 5 hours, whereupon absorption of hydrogen ceases. The catalyst is filtered off and the aqueous filtrate is distilled at 40 mm Hg over a water-bath heated to 50°C. The residue distills at 105°C. under 0.5 mm Hg to yield a principal fraction of pure caprolactam. The lactam purified in this manner yields a polymer colour rating of 80 to 100 when determined in the manner described in Example 1.

On hydrogenation in a neutral solution, i.e., without addition of sodium hydroxide, the polymer colour rating of the original lactam cannot be improved and amounts to more than 350.

EXAMPLE 23

100 parts of a crude caprolactam, obtained according to a process described in British Patent Specification 904,302 by the reaction of nitrosyl sulfuric acid in oleum with cyclo-

hexane carboxylic acid, are dissolved in 120 parts water and, after the addition of sodium hydroxide and 3 parts Raney nickel shaken with hydrogen at room temperature under normal pressure. The absorption of hydrogen ceases after 15 minutes. The catalyst is filtered off and the water removed by distillation over a water-bath at 50°C. and 14 mm Hg pressure; the lactam is then distilled at 105°C. under 0.5 mm Hg. After running off the first 2.2 parts, 96.3 parts pure lactam are obtained as the principal fraction and correspond to a yield of 96.3% referred to the initial, impure lactam. The polymer colour rating of the purified lactam lies between 40 and 60.

#### EXAMPLES 24 to 31

These examples are presented in Table 2. These experiments were carried out in a manner analogous to that of Example 23, and in each case 50 parts of a once-distilled caprolactam are dissolved in 100 parts.

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TABLE 2

| Example No. | Catalyst (Parts)     | Base (Parts) | Hydrogen Pressure in Atm. | Temperature in °C. | Reaction Time in Hrs. | Polymer Colour Rating |
|-------------|----------------------|--------------|---------------------------|--------------------|-----------------------|-----------------------|
| 24          | 3 Raney Ni           | 1 NaOH       | 1                         | 20                 | 1                     | 60—80                 |
| 25          | 3 Raney Ni           | 0.5 KOH      | 1                         | 20                 | 1                     | 60—80                 |
| 26          | 1 Raney Ni           | 0.5 NaOH     | 100                       | 20                 | 12                    | 40—60                 |
| 27          | 0.5 PtO <sub>a</sub> | 1 NaOH       | 1                         | 60                 | 1                     | 60—80                 |
| 28          | 0.5 PtO <sub>2</sub> | 1 NaOH       | 100                       | 60                 | 6                     | 40—60                 |
| 29          | 1 Ru on carbon (5%)  | 1 NaOH       | 1                         | 60                 | 1                     | 40—60                 |
| 30          | 1 Pd on carbon (5%)  | 1 NaOH       | 1                         | 60                 | 1                     | 40—60                 |
| 31          | —                    | 1 NaOH       | —                         | 60                 | —                     | 350                   |

**EXAMPLE 32**

80 parts of a once - distilled caprylolactam prepared by the Beckmann conversion of cyclo - octanone oxime hydrochloride (obtained by photo - oximation) with sulfuric acid, are dissolved in water and, after the addition of 2 parts sodium hydroxide and 2 parts Raney nickel, shaken with hydrogen at room temperature and under normal pressure. 120 parts by volume hydrogen are taken up in 90 minutes, whereupon absorption ceases. After filtering of the catalyst, the water is removed by distillation over the water bath at 50°C. and under a pressure of 50 mm Hg. On distilling the residue, 2.5 parts, consisting essentially of caprylolactam are then distilled off as a principal fraction at 112°C. under 0.5 mm Hg, this represents a yield of 95.5 percent referred to the initial, impure lactam. The caprylolactam purified in this manner has a polymer colour rating of 60 to 80, whereas the initial material had a rating

of more than 350 even after a further distillation, but without special treatment.

If the charge is not treated with hydrogen, or if hydrogenation is carried out without addition of alkali, or if the base is added only after hydrogenation, and if the procedure then follows the course given above, no improvement in the polymer colour rating can be detected.

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**EXAMPLES 33 to 42 and 43 to 61**

A series of experiments are presented in Tables 3 and 4; these were carried out with caprylolactam in the manner described in the previous example. Table 3 demonstrates the dependence of the method of purification on the type and quantity of base added. In each case, 50 parts lactam in 100 parts water were shaken with hydrogen in the presence of 3 parts Raney nickel at 20°C. under normal pressure. The average absorption of hydrogen was 100 parts by volume.

TABLE 3

| Example | Base (Parts)   | Polymer Colour Rating |
|---------|--|-----------------------|
| 33      | 3 KOH  | 40—60                 |
| 34      | 3 NaOH   | 40—60                 |
| 35      | 0.5 NaOH   | 60—80                 |
| 36      | 0.3 NaOH   | 40—60                 |
| 37      | 0.2 NaOH   | 100                   |
| 38      | 3 CaO  | 150                   |
| 39      | 3 CaCO <sub>3</sub>                                  | 150                   |
| 40      | 3 Ba(OH) <sub>2</sub>                                | 80                    |
| 41      | 1.5 conc. ammonia (25%)                              | 60—80                 |
| 42      | 0.73 N (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> | 100                   |

The following Table 4 demonstrates the dependence of the catalyst on the conditions of use. In each case 50 parts lactam in 100

parts water, and in the presence of 0.5 parts sodium hydroxide, are treated with hydrogen under the conditions described in Example 32.

TABLE 4

| Example No. | Catalyst (Parts)                | Hydrogen Pressure in Atm. | Temperature in °C. | Reaction Time in Hrs. | Polymer Colour Rating |
|-------------|---------------------------------|---------------------------|--------------------|-----------------------|-----------------------|
| 43          | 0.5 Raney Ni                    | 1                         | 20                 | 1                     | 40—60                 |
| 44          | 1 Pd on carbon (5%)             | 1                         | 20                 | 1                     | 80                    |
| 45          | 0.5 PtO <sub>2</sub>            | 1                         | 20                 | 1.25                  | 100—150               |
| 46          | 0.5 PdO                         | 1                         | 20                 | 1                     | 100                   |
| 47          | 0.5 PtO <sub>2</sub>            | 1                         | 60                 | 0.25                  | 40—60                 |
| 48          | 1 Ru on carbon (5%)             | 1                         | 60                 | 1                     | 60—80                 |
| 49          | 1 Ni on carbon (5%)             | 1                         | 60                 | 1                     | 150                   |
| 50          | 1 Pd on carbon (5%)             | 1                         | 60                 | 0.5                   | 60—30                 |
| 51          | 1 Pd on CaCO <sub>3</sub> (5%)  | 1                         | 60                 | 1                     | 100—150               |
| 52          | 1 Pd on magnesium silicate (5%) | 1                         | 60                 | 1                     | 150                   |
| 53          | 1 Ni on carbon (5%)             | 50                        | 20                 | 6                     | 60                    |
| 54          | 1 Pd on CaCO <sub>3</sub> (5%)  | 50                        | 20                 | 2                     | 40—60                 |
| 55          | 1 Pd on magnesium silicate (5%) | 100                       | 20                 | 12                    | 40—60                 |
| 56          | 1 Pd on BaSO <sub>4</sub> (5%)  | 100                       | 20                 | 1                     | 60—80                 |
| 57          | 1 Pt on BaSO <sub>4</sub> (5%)  | 100                       | 20                 | 12                    | 80—100                |
| 58          | 1 Ni on MgO (5%)                | 100                       | 20                 | 2                     | 100—150               |
| 59          | 1 Pt on BaSO <sub>4</sub> (5%)  | 100                       | 60                 | 1                     | 40—60                 |
| 60          | 1 Ni on MgO (5%)                | 100                       | 60                 | 12                    | 80—100                |
| 61          | 0.5 Ni on MgO (5%)              | 200                       | 100                | 2                     | 40—60                 |

**EXAMPLE 62**

50 parts of a  $\gamma$ -laurolactam, which has been prepared by the Beckmann conversion of cyclododecanone oxime hydrochloride, and  
 5 which has a polymer colour rating of 350 and whose purity cannot be improved by sublimation, are dissolved in 80 parts methanol and, after adding 1 part sodium hydroxide and 1 part palladium on activated carbon  
 10 (5%), are shaken up with hydrogen for 6 hours in a bomb at 60°C. under a pressure of 100 atmospheres. After filtering off the catalyst, the methanol solution is poured into 200 parts water, whereupon the laurolactam  
 15 separates out quantitatively. The lactam is filtered and, after drying, is sublimed at a pressure of 0.5 mm Hg the temperature of the bath being 180 to 190°C. The sublimate consists of 48.7 parts laurolactam, corresponding to a yield of 97.4 percent referred  
 20 to the initial, impure lactam. After polymerizing a specimen of the sublimate for 20 hours at 270°C. with 3% hexamethylene di-ammonium adipate in the manner described in  
 25 Example 1, the polymer colour rating was 40 to 60.

Similar success can be obtained by employing a 50 percent aqueous methanol or ethanol as the solvent instead of pure methanol.

**30 WHAT WE CLAIM IS:—**

1. A process for purifying a lactam having

4 to 12 carbon atoms by treatment with hydrogen which process comprises contacting the lactam either dissolved in an inert solvent or liquefied, in the presence of basic reacting substances, with nascent hydrogen formed *in situ*, or with molecular hydrogen in the presence of a hydrogenating catalyst under such conditions that the lactam is substantially unattacked.

35

2. A process as claimed in Claim 1, wherein the basic reacting compound is used in an amount of 0.01 to 20% by weight with reference to the lactam.

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3. A process as claimed in Claims 1 and 2, wherein purifying is carried out at a temperature between -15 and +250°C.

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4. A process as claimed in Claims 1 to 3, wherein the lactam used is dissolved in a solvent and forms a 20 to 80% by weight solution.

50

5. Lactams purified by a process as claimed in any of the foregoing claims.

6. A process for purifying lactams as claimed in claim 1, substantially as described in the foregoing Examples.

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J. Y. & G. W. JOHNSON,  
 Furnival House, 14-18, High Holborn,  
 London, W.C.1,  
 Chartered Patent Agents,  
 Agents for the Applicants.

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